A Novel Synthesis and Characterization of Copper Chloride Nanocrystals in a Sodium Chloride Matrix

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Introduction

Quantum dots are tiny crystals of semiconductor material that exhibit special optical properties which are attributed to their size. As semiconductors, the materials from which quantum dots are made generate pairs of electrons and holes on interaction with light of sufficient energy. However, as opposed to the bulk semiconductor material, the quantum dots serve to confine the electron-hole pair to a tiny physical space and in all three dimensions. The effect of this confinement is an alteration of the quantum mechanical properties of the semiconductor, most notably an increase in the band gap energy. The confinement of the electron-hole pairs, or excitons, produces the unique optical properties of quantum dots such as shifted fluorescence output. These quantum confinement effects are observed in systems typically comprised of several hundred to several thousand individual atoms and an overall crystal dimension of a few nanometers. A typical quantum dot system comprised of cadmium selenium nanocrystals, produced during the course of this research, is shown in Figure 1 under incandescent light (bottom) and under broad spectrum ultraviolet illumination with a peak wavelength of 312 nanometers (top). The impact of quantum confinement of the excitons within the semiconductor material is evident in the shifting photoluminescent output of the quantum dots under ultraviolet illumination. Nanocrystals small enough to confine the excitons present in the cadmium selenium material produce a larger bandgap, visible as a shift from the red side of the visible spectrum toward the blue side of the visible spectrum. It is important to note that the nanocrystals contained in each vial are made of the exact same material. Only the differing size of the crystals, from a radius of about 1.2 nanometers (left) to 5.0 nanometers (right), changes the color. It is this ability to "tune" the photochemical properties of quantum dots by growing nanocrystals of differing sizes but from the exact same material that makes them attractive for use in a multitude of important application. However, the highly toxic nature of the materials required for synthesis of quantum dots, the advanced synthetic techniques and complicated equipment needed are all major disadvantages. The desire to overcome these limitations and produce safe, inexpensive, easily synthesized, non-toxic quantum dots then became the goal of the research.

CdSe Nanocrystals

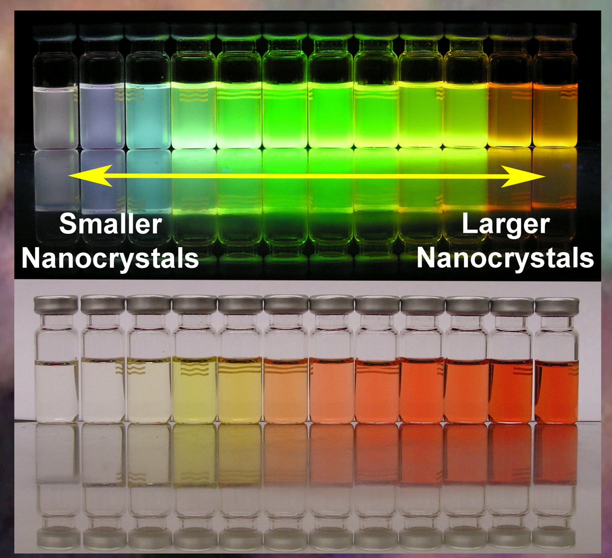

Figure 1 - Quantum confinement is demonstrated as flourescence output shifts to higher energies with decreasing radius.

Typical Rapid Synthesis Scheme

Figure 2 - A typical rapid synthesis is carried out over an assembly of three Fisher burners supplied with methane.

Synthesis

Sodium chloride becomes molten at around 801 ºC, a temperature reachable with common lab gases such as methane or propane, enabling basic synthesis on the benchtop from the molten phase. In assembling three Fisher burners as shown in Figure 2, a small quantity of ACS grade sodium chloride became completely molten in a covered ceramic crucible in short period of time. Once molten, the lid of the crucible was removed and a small amount of copper was introduced to the melt from the solid phase. Chemical activity was observed with the immediate removal of oxides from the solid-phase copper. After stirring to allow for complete interaction the solution was covered once more and the melt allowed time to become completely molten once more. After a short period the crucible was removed from heat and allowed to cool slowly over an extended period. Once cooled to room temperature the product was collected by placing the crucible upside down on the bench and striking it with a hammer until the product fell free or the crucible was broken apart. Observations of product physical characteristics were noted and variations in the amount of copper; the size and shape of the copper; time of sodium chloride exposure to copper; amount of sodium chloride; heating and cooling rates; temperatures; and other variables were adjusted to facilitate desired product attributes.

Representative Sample from Bulk Product

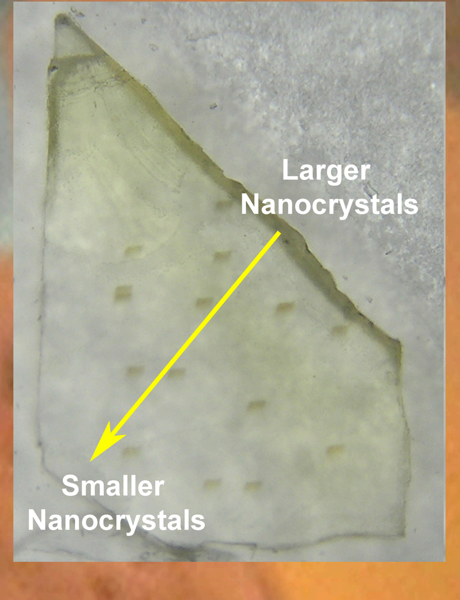

Figure 3 - A faint yellow gradient appears in a slice taken from the center to the outer edge of a cylindrical parent crystal. SAXS probe points are visible.

Photoluminescence

Observed photoluminescence of the product was quantified using a custom, purpose-built spectrometer. The sample was secured in an Abbess Instruments transverse optical cryostat charged with liquid nitrogen, equipped with dual orthogonal sapphire windows and maintained at 90K as indicated by properly calibrated, dual silicon diode cryosensors coupled to a LakeShore 330 temperature controller. The sample was illuminated with light from a 150 W high-pressure Xenon source profiled with 1 mm slits, passed through a .25 m folded Czerny-Turner monochromator tuned to 325 nm and focused to a spot comparable in size to the SAXS probe beam using dual cylindrical quartz optics. Fluorescence emission from the sample was collected with quartz optics placed orthogonal to the excitation source and channeled into an automated 0.85 m dual Czerny-Turner monochromator with 2400 line/mm gratings blazed for 400 nm and profiled with four sets of 1 mm slits located at the input and output of each of the monochromators. Optical signals were detected with a Hamamatsu R928 photomultiplier tube biased at 600 VDC and housed in a refrigerated enclosure at 253K. Noise reduction was achieved using a Stanford Research Systems optical chopper operating at 1 kHz and an SR850 DSP Lock-In Amplifier. As indicated in Figure 4, the collected spectra each indicate a fluorescence peak of the Z_3 exciton, a known structure present in bulk copper chloride and generally located near 388 nm.

Small Angle X-Ray Scattering

The small angle X-ray scattering (SAXS) portion of the investigation was carried out at the Advanced Photon Source at Argonne National Laboratory on beamline 12-ID-B. The beam energy was approximately 12 keV and collimated to a spot size approximately 1 mm x 2 mm at the sample. A 2 cm square tantalum plate with a 2 mm central orifice was positioned immediately prior to the sample in the space between the sample and the incoming X-rays to reduce noise from air scattering. Crystalline samples were mounted in Laue configuration via Scotch tape secured across a small wire-form apparatus atop an automated two-axis stage. For further noise reduction, immediately following the sample was placed a large vacuum chamber which occupied the entire space between the sample and the detector. The detector used was a Dectris Pilatus 2M, an advanced reverse-biased silicon diode array detector with exceptionally low background noise and single-photon sensitivity, located approximately 2 m from the Laue experiment. Samples were exposed to X-ray energy for approximately 10 s and data sets were collected as rastered lines across large regions in an effort to expose nanocrystal size gradients within the parent crystal. Two dimensional diffraction images were collected in TIFF format from the detector and reduced automatically by Matlab routines. Data was further processed using Igor Pro 6.22A with software macros Nika, Irena and Indra for further reduction, analysis and presentment.

Z_3 Exciton Fluorescence

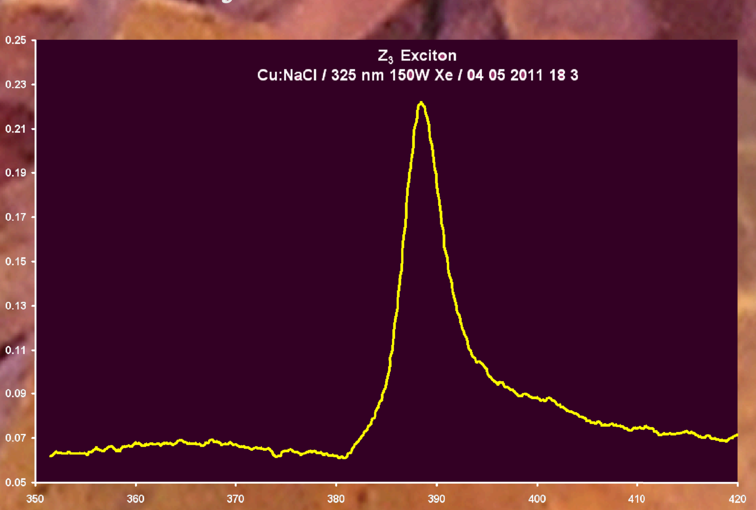

Figure 4 - The fluorescence peak of the Z_3 exciton present in copper chloride bulk product is present in the representative sample in Figure 3.

Electron Microscopy with Energy Dispersive X-Ray Spectroscopy

Log / Log Plot of Intensity v. q

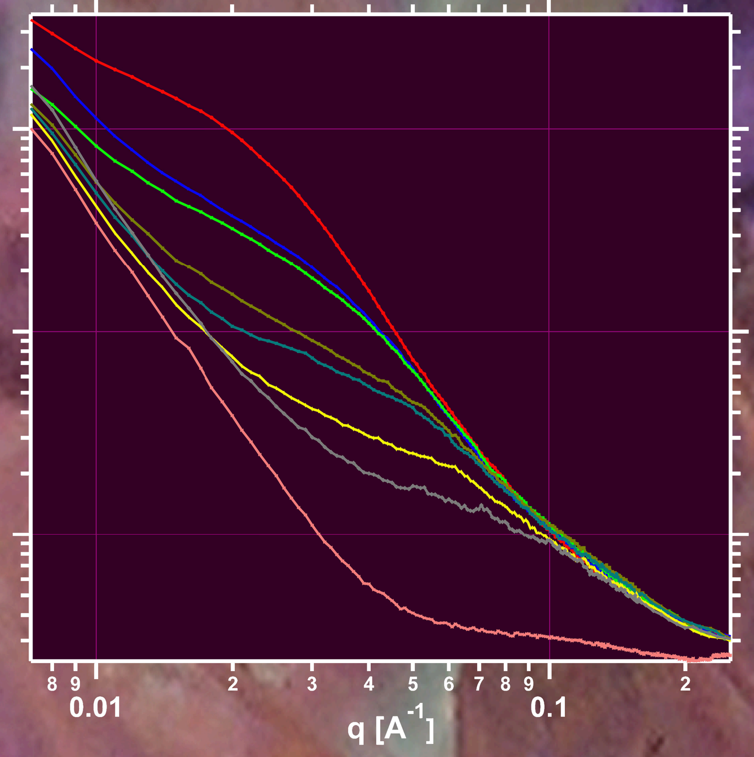

Figure 5 - SAXS data obtained from rastered points across the representative sample in Figure 3. Peaks from large nanocrystals appear in the upper left while peaks from smaller nanocrystals appear in the lower right.

The transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS) portions of this work were performed at the Center for Functional Nanomaterials at Brookhaven National Laboratory. The electron micrograph illustrated in Figure 7 was collected on a JEOL JEM-1400 Low Voltage TEM operated at 120kV with smallest possible objective and condenser apertures, spot size 3 and captured using a Gatan 2048 x 2048 pixel CCD camera coupled to Gatan DigitalMicrograph software for archival and analysis. Selected representative samples were cleaved and ground to sub-micron size in a purpose-built automated agate ball mill with agate grinding media. Ground samples were immersed in hexanes and sonicated for approximately twenty minutes in a scintillation vial prior to introduction to the TEM grid. The TEM grids used were Ted Pella Lacey Carbon, 200 mesh, Nickel substrate. Sample introduction was achieved by dipping the TEM grid in the settled hexanes solution and secured with drying by heat lamp. TEM grids were mounted in a Gatan Cryoholder which had been processed for use on a Gatan 655 Turbo Pumping Station and equipped with a Gatan Model 900 SmartSet temperature controller. Once introduced to the TEM column samples were cooled and maintained at 77K for the duration of the imaging cycle to reduce beam damage. The EDS spectrum illustrated in Figure 8 was collected using a JEOL JEM-2100F HRTEM equipped with an Oxford Energy TEM 250 EDS operated in single spectrum mode with probe size 2 nm. EDS data was analyzed using the INCA Microanalysis System.

Combined Log / Log Plot of Intensity v. Q, Diameter and Size Distribution

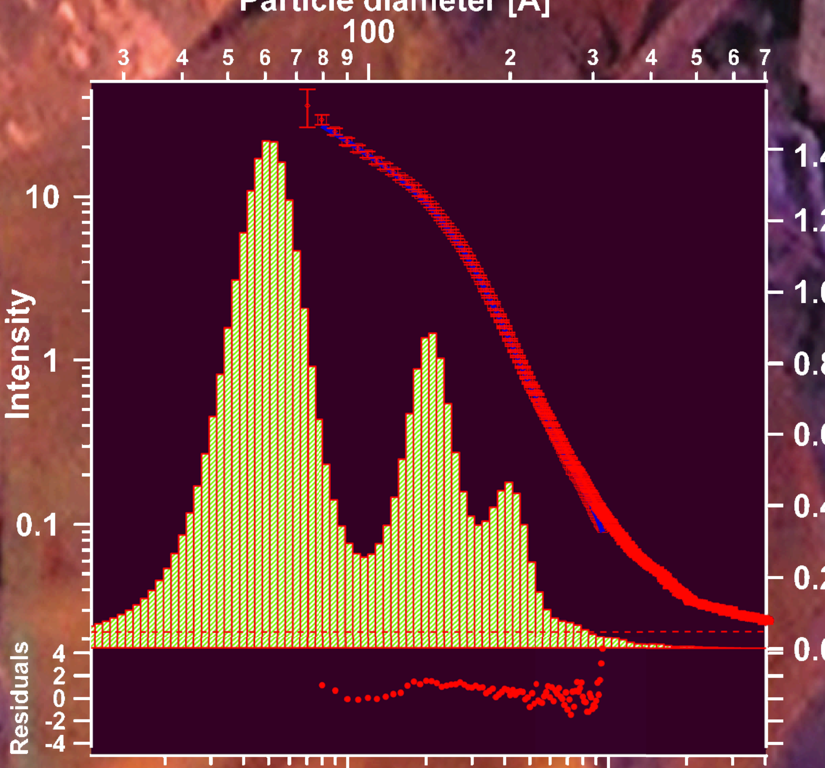

Figure 6 - The uppermost SAXS plot from the previous series analyzed for particle size and volume distribution. Predominant nanoparticle sizes are 6 nm, 15 nm and 20 nm.

Conclusion

The applied research question which began this work focused on the possibility of replacing complicated, expensive and highly toxic semiconductor quantum dots with a simple, non-toxic equivalent. The empirical evidence suggests this possibility exists. The photoluminescence spectrum collected from the representative sample indicates a strong peak near 388 nm, a telltale sign of the Z_3 exciton known in copper chloride bulk material. The SAXS analysis of the same sample indicates order consistent with spherical nanocrystals of particular sizes distributed throughout the sample volume. The TEM micrograph of the same representative sample indicates spherical morphology of nanoparticles in the same size regimes and relative abundances indicated by the SAXS analysis. The EDS spectrum collected on a single nanocrystal isolated from the same sample indicates a composition of 1:1 copper to chlorine. Based on these observations we are inclined to conclude that the bulk sodium chloride crystal contains non-toxic, easily synthesized nanocrystalline copper chloride quantum dots which mimic their highly-toxic and sophisticated counterparts.

TEM Micrograph

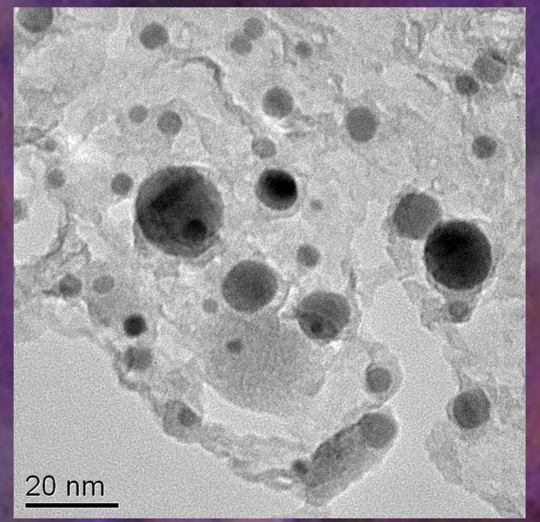

Figure 7- TEM micrograph or representative sample confirms SAXS measurements of CuCl nanocrystals and indicates spherical morphology.

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EDS of TEM Specimen

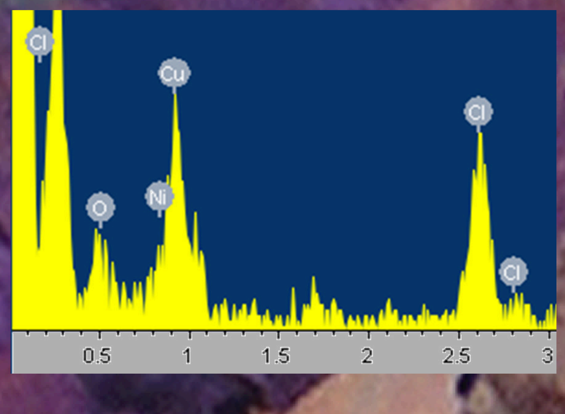

Figure 8 - EDS peaks collected from a single nanoparticle indicate an approximate 1:1 ratio of copper to chlorine and suggest CuCl as the empirical formula.

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